

Physico-Chemical Determinations at High Pressures by Optical Methods.

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(Abstract.)

Apparatus for Optical Measurements at High Pressures.

The apparatus consists of three chief units:—

- (1) Plant for the production and measurement of pressures up to 4000 kgm./cm.².
- (2) A "pressure-bomb" to hold the substances under investigation.
- (3) An optical bench for observations in polarised light, and for measurements of the change of refractive index, dispersion, rotatory power, absorption, double-refraction and optical-axial-angle, by pressure.

The "pressure-bomb" is fitted with two "windows" of boro-silicate glass (Jena); these have the shape of truncated cones, are 20 mm. thick, rest with the base upon a flat ring-shaped washer of vulcanised fibre, and are surrounded by a conical mantle of ebonite, the washers and ebonite mantles thus preventing an immediate contact of the glass and steel surfaces. The chief object of using these washers and conical packings may be described as being that of keeping the glass constantly surrounded by a half-plastic mass, which flows slightly, and thus transmits the pressure to the glass body as evenly as possible. The pressure-bomb has been tested under high pressures, both at liquid air temperatures and at temperatures up to 150°. At ordinary temperatures the glass windows have, under favourable circumstances, withstood pressures of over 4000 kgm./cm.² without being injured in any way.

Optical Determinations of Diagrams of State.

Melting-points and transition-points between different crystalline modifications may be determined either at constant pressure by altering the temperature, or at constant temperature by altering the pressure. Crystallisation and melting at constant temperature, "isothermal crystallisation" and "isothermal melting," are of special interest, as it is possible not only to study the crystallisation, melting, and supercooling phenomena more in detail than under ordinary conditions when the transition is effected by temperature change, but it is also possible to study the phenomena connected with superheating of the crystalline phase.

The Diagram of State of Carbon Tetrabromide, CBr₄.

The melting-point of CBr₄ is raised 1° by a pressure of only 16 kgrm./cm.². The transition-point from monoclinic to regular crystal-form is raised 1° by 32 kgrm./cm.². The melting-point curve and the transformation-point curve do not, therefore, intersect at high pressures to form a triple-point. In consequence, the anisotropic monoclinic form of carbon tetrabromide cannot be caused to melt at any temperature or pressure whatever.

The Diagram of State of α - β -Dibrompropionic Acid, CH₂Br.CHBr.COOH.

Beside the stable modification of the acid, melting at 64°, an unstable modification exists, melting at 51°. Both forms crystallise in the monoclinic system. As the unstable modification is not spontaneously transformed into the stable one so readily as in most other cases of "monotropy," and only very small quantities are employed for an optical investigation, it has for the first time been possible in this case to determine the melting-point curve of an unstable modification also.

The velocity of crystallisation, and also of melting, of both modifications is small, and it has therefore been possible to determine the limits within which not only supercooling, but also superheating, can be effected at different pressures. During isothermal melting of the unstable modification, the pressure may be reduced as much as about 150 kgrm./cm.² below the true melting-point pressure before melting takes place with almost instantaneous velocity. This pressure, 150 kgrm./cm.² below the melting-point pressure, corresponds to a superheating of nearly 3°.

The melting-point of the stable modification is raised 1° by a pressure of 51.28 kgrm./cm.², and that of the unstable modification 1° by a pressure of 53.48 kgrm./cm.². The melting-point curves run further apart as the pressure increases, and the modification unstable at ordinary pressures thus remains unstable at all pressures.

The two melting-point curves, of which the upper one has been traced over a pressure range of 1060 kgrm./cm.², and the lower one over a pressure range of 1330 kgrm./cm.², are perfectly straight lines. If we continue these melting-point lines towards negative pressure, we find that they intersect at a point corresponding to a temperature of between -270° and -280°, that is, at the absolute zero. At any pressure, the difference between the absolute melting-points of the two modifications is therefore similar to the difference of the absolute melting-points at ordinary pressure.

This work has been executed at the Davy-Faraday Laboratory of the Royal Institution during the past year.